

L120,284



# PATENT SPECIFICATION

DRAWINGS ATTACHED

L120,284

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## COMPLETE SPECIFICATION

### Separation and Purification of Acrylic Acid

We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, a Corporation organised under the Laws of Japan, of 25—1, Dojimahamadori-1-chome, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the separation and purification of acrylic acid from mixtures thereof with acetic acid and water.

A number of researches have been made on a method for producing acrylic acid by vapour phase oxidation of propylene or acrolein. However, researches on refining acrylic acid so produced have been relatively rare. Generally, in the crude acrylic acid produced by the aforesaid vapour phase oxidation, acetic acid is present as a by-product in a molar proportion in the range 1/4 to 1/500 based on the acrylic acid. Accordingly, from an industrial point of view the separation of acetic acid from acrylic acid mixtures containing the same is important to produce pure acrylic acid. Only a few such separation methods have hitherto been proposed, including those disclosed in British Patent Specifications Nos. 997,324 and 997,325. Those methods comprise cooling the product obtained by vapour phase oxidation of propylene or acrolein, absorbing the product in water to obtain an aqueous solution of acrylic acid containing acetic acid, and evaporating water therefrom. Alternatively, the aqueous solution of acrylic acid is extracted by adding a suitable solvent thereto to extract acrylic acid as well as acetic acid and the resulting extract is distilled to separate the solvent from acrylic acid containing acetic acid, and then acetic acid is removed by distillation under reduced pressure to obtain pure acrylic acid.

Another method which has been proposed is to add a suitable solvent capable of extracting only acrylic acid, to obtain an aqueous

solution of acrylic acid. That method, however, requires a large amount of solvent and there is a considerable loss of acrylic acid accompanied by a loss of the solvent.

In the aforesaid distillation, the specific volatilities of acrylic acid and acetic acid are so small that a large number of plates are required in the distilling column and the reflux ratio must be high. These measures are disadvantageous for practical application on an industrial scale. Moreover, since acrylic acid is easily polymerized, the separation is generally carried out in the presence of a polymerization inhibitor. Even then, so-called popcorn polymerization often occurs and causes a blockage in the distilling column. The greater the number of plates, the greater is the likelihood of such blockage. It is therefore desirable to decrease the number of plates where acrylic acid is present in a high concentration, but in the binary system of acrylic acid and acetic acid the number of plates where acrylic acid is present in a high concentration within the distilling column must necessarily be large due to the relation between the specific volatilities of acetic acid and acrylic acid and the concentrations.

The present invention is based on the appreciation that pure acrylic acid can be obtained efficiently by adding an entrainer which forms an azeotrope with acetic acid. That is to say, acetic acid can readily be separated from acrylic acid by distillation when an entrainer capable of forming an azeotropic mixture with acetic acid is present. The entrainer comprises at least one of a first class of substances (hereinafter termed "the first component") and at least one of a second class of substance (hereinafter termed "the second component"). The first component consists of aliphatic or alicyclic hydrocarbons having 7 carbon atoms and toluene. The second component consists of water, esters of the formula  $R_1COOR_2$  wherein  $R_1$  is a hydrocarbyl radical having 1—3 carbons and  $R_2$  is a hydrocarbyl radical

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having 1—4 carbons and the boiling point of which does not exceed 130°C and nitriles having 3 or 4 carbon atoms.

In the first component only were used as an entrainer in the azeotropic distillation, the first component would form an azeotropic mixture with acrylic acid but in a small amount. Accordingly, a part of the acrylic acid would necessarily be distilled out when distilling the acetic acid. However, when the second component is added to the first component, substantially no acrylic acid enters the acetic acid distillate. The mixing ratio of the first component to the second component is 1 mol of the former to 0.05—1.5, preferably 0.2—1.5, moles of the latter.

The first component is selected so as to form an azeotropic mixture with acetic acid but not with acrylic acid; n-heptane is desirable as an aliphatic hydrocarbon of seven carbon atoms for industrial application. If the number of carbon atoms in this component were 6 or less, an azeotropic mixture with acetic acid would not be formed; conversely, if the number of carbon atoms were more than 8 the separation of acetic acid from acrylic acid would become difficult.

The amount of the second component to be added is not less than 0.05 mol per 1 mol of the first component. If it were to exceed 2.0 moles would it restrain the action of the first component that hardly any acetic acid would be distilled from the head of the column. For practical purposes the effective limits are from 0.2 to 1.5 moles.

Ketones and ethers have a similar effect as the second component, but are not suitable because acrylic acid is not stable and easily polymerizes in the presence of such compounds. From the industrial point of view, ethyl acetate, methyl acrylate, propyl acetate, ethyl acrylate, acetonitrile, acrylonitrile and water are preferred as the second component.

In the performance of azeotropic distillation by the use of the entrainer consisting of the first and second components, in order to avoid the polymerization of acrylic acid it is essential to carry out the distillation under a reduced pressure of less than 350 mmHg-abs, and in the presence of a polymerization inhibitor, for example, hydroquinone, hydroquinone monoethyl ether, phenothiazine or oxygen.

The entrainer may be introduced into the column from the head as in the conventional azeotropic distillation, or into an enriching section of the column or into the feed. Alternatively, a part or all of the first component may be mixed into the feed and a part or all of the second component introduced from the head of the column, i.e. not only from one place but also from two places or more.

In the distillation according to the present invention the distillate azeotrope does not always form two liquid layers. When the dis-

tillate azeotrope does not form two liquid layers, acetic acid may be removed therefrom by extraction with water or acetonitrile or neutralization or esterification or by other known methods. The remaining liquor from which acetic acid has been removed can be recycled for use again as an entrainer.

In a process for the production of acrylic acid by the vapour phase oxidation of propylene or acrolein, usually not more than 40% by weight (e.g. 10—30%) of a crude aqueous acrylic acid solution is obtained which contains acetic acid in a molar ratio of from 1/4 to 1/500, based on the acrylic acid. In such a case the aqueous solution can be dealt with by a combination of solvent extraction and azeotropic distillation. Thus, the crude acrylic acid solution containing acetic acid is first contacted beforehand with a mixed solvent consisting of the first and the second components (excluding those which are water-soluble, for example, water, acetonitrile and methyl acetate) to extract acrylic acid from the crude solution and then the extract is distilled. In this way the acetic acid as well as the solvent can be distilled out from the top of the distillation column while acrylic acid free from acetic acid is obtained from the bottom. The solvent may be recycled with or without first removing acetic acid from it. When the solvent containing acetic acid is re-used, provision must be made to ensure that acetic acid does not accumulate excessively, by removing from the system an amount of acetic acid corresponding to that introduced in the starting aqueous solution. If water, acetonitrile and/or methyl acetate, which are soluble in water, were used as the second component of the solvent, they would be removed from the solvent system along with the acetic acid, which is why such second components of the solvent should not be used when the solvent is recycled.

In the composition of the feed liquor to the distilling column (hereinafter referred to as the solvent separation column) where the solvent is removed, the mol ratio of the second component/the first component must be from 0.05:1 to 1.5:1, preferably from 0.2:1 to 1.5:1. Therefore, when the solvent is introduced into the contacting column (hereinafter referred to as the extraction column) where acrylic acid is extracted, the mol ratio of the second component/the first component in the extraction solvent is determined so as to be within the range 0.05:1 to 1.5:1, preferably 0.2:1 to 1.5:1. In the solvent having the composition thus determined, the extraction of acrylic acid may become insufficient in some cases, according to the kind of solvent. In such a case, the insufficiency of extraction can be overcome by increasing the proportion of the second component, which is only sparingly soluble in water. However, difficulty often occurs in distilling out all of the acetic acid

from the head of the solvent separation column when the proportion of the second component in the composition of the feed of the solvent separation column is increased too much. To avoid this difficulty a dehydrating tower may be introduced between the extraction column and the solvent separation column to distil out a part or all of the water or a part of the solvent so as to restore the mol ratio of the second component/the first component of the tower bottom liquor of the dehydrating tower to within the range 0.05:1 to 1.5:1, preferably 0.2:1 to 1.5:1. The resulting liquor is then fed to the solvent separation column.

An embodiment of the invention will now be described by way of example with reference to the accompanying drawing, which is a diagram of this embodiment.

An aqueous acrylic acid solution containing acetic acid is introduced through a line *a* into the top of an extraction column 1, and an extraction solvent comprising the first component, the second component and a small amount of acetic acid is introduced counter-currently through a line *f*. An extract liquor containing acrylic acid and acetic acid passes out through a line *b*. The weight ratio of the feed liquor introduced through *a* to the extraction solvent introduced through *f* is in the range 1:0.6 to 1:5, preferably 1:0.8 to 1:3.

The extract liquor is dehydrated in a dehydrating tower 3 and then fed through a line *g* into a solvent separation column 4. The dehydrating tower may be operated under normal pressure or reduced pressure. The distillate forms two liquid layers, an aqueous layer and an oily layer, of which only the oily layer refluxes to the tower. In the solvent separation column 4 the distillation is carried out under a reduced pressure of less than 350 mmHg-abs. in order to avoid polymerization due to an increase in the concentration of acrylic acid in the column. Acrylic acid substantially free from acetic acid is withdrawn from the solvent separation column 4 through a line *i*. Distillate from the solvent separation column withdrawn through a line *j*, distillate from the dehydrating tower 3 withdrawn through a line *h*, recovered solvent withdrawn through a line *e* from a solvent recovering column 2 and a make-up for a lost solvent introduced through a line *k* together constitute the extraction solvent introduced through the line *f*. The recycled and make-up solvents may be returned to the extraction column 1 all together or individually; in the latter case *f* would represent all the separate lines. As to the behaviour of acetic acid contained in the solvent introduced from *f*, when the operation

settles down to a steady state a constant amount of acetic acid is continuously recycled from *b* to *f* passing through *j*, whereby the removal of acetic acid contained in the feed liquor can be continuously carried out, because the same amount of acetic acid is contained in the residue removed from the extraction column 1 through the line *c* and is introduced in the feed to the column. The residue from the extraction column is introduced through the line *c* into the solvent recovery column 2, thereby recovering the solvent contained in the residue. A diluted aqueous solution of acetic acid is removed through a line *d*. Acetic acid can, if desired, be recovered from this solution by any suitable known method.

In order to prevent the polymerization of acrylic acid in each stage a polymerization inhibitor, for example hydroquinone, phenothiazine or oxygen, is used.

The extraction column 1 may be, for example, a mixer-settler, a packed column, a perforated plate column, a column having rotating blades or a pulsed column. Furthermore, the continuous phase of the extraction column may be either an aqueous phase or an organic phase. The extraction temperature is preferably from 0° to 60°C. In some cases three liquid phases may be formed, depending on factors such as the relationship between the first component and the second component which is sparingly soluble in water, the relative proportions of these components and the concentration of acids. In such a case, restoration of only two liquid phases can conveniently be carried out by elevating the temperature or replacing up to three tenths of the first component with benzene.

The following Examples illustrate the invention. All ratios, percentages and proportions in the Examples and elsewhere are by weight unless otherwise indicated.

#### EXAMPLE 1

A solution consisting of ethyl acetate, n-heptane, acetic acid, acrylic acid and a little water was pumped at a rate of 20 g/hr. into the middle zone of a triple tubular glass distilling column 2000 mm high and 20 mm in diameter. The column was packed with coiled packing pieces each 5.5 mm in diameter and 3.5 mm in length.

Azeotropic distillation was continuously carried out under an operating pressure of 175 mmHg, with the reflux ratio of 1.1, at a column bottom temperature of 99°—101°C and a column head temperature of 41°—45°C.

Distillation of feeds having various compositions were carried out and the results obtained were as shown in the following Table.

TABLE

Experiment No.	Composition (% by weight)							<i>b/c</i> (weight ratio)	Mol ratio in a EtAc/ n-Hep
		EtAc	n-Hep	HAc	HACr	Water	Other heavy substances		
1	<i>a</i>	37.9	33.2	3.5	25.4	—	0	2.94	1.3
	<i>b</i>	50.9	44.5	4.6	0	—	0		
	<i>c</i>	0	0.1	0.2	99.0	—	0.7		
2	<i>a</i>	46.1	35.2	2.3	16.5	—	0	5.06	1.5
	<i>b</i>	55.1	42.1	2.73	0	—	0		
	<i>c</i>	0	0	0.1	99.4	—	0.5		
3	<i>a</i>	21.2	60.5	2.2	15.9	—	0	5.28	0.4
	<i>b</i>	25.2	72.1	2.6	0	—	0		
	<i>c</i>	0	0	0.1	99.4	—	0.5		
4	<i>a</i>	14.5	40.9	5.4	39.1	—	0	1.56	0.4
	<i>b</i>	28.9	67.4	8.7	0	—	0		
	<i>c</i>	0	0	0.3	99.2	—	0.5		
5	<i>a</i>	32.7	21.7	5.6	40.0	—	0	1.47	1.7
	<i>b</i>	55.2	36.6	8.15	0	—	0		
	<i>c</i>	0	0	1.8	97.7	—	0.5		
6	<i>a</i>	9.0	45.0	6.0	40.0	—	0	1.54	0.22
	<i>b</i>	14.8	74.2	9.8	1.2	—	0		
	<i>c</i>	0	0	0.1	99.8	—	0.4		
7	<i>a</i>	22.9	43.6	3.8	27.4	2.3	0	2.65	0.6
	<i>b</i>	31.6	60.1	5.1	0	3.07	0		
	<i>c</i>	0	0.1	0.4	99.0	0.08	0.4		
8	<i>a</i>	33.9	33.8	3.6	28.0	0.7	0	2.61	1.1
	<i>b</i>	47.2	47.1	4.9	0	0.8	0		
	<i>c</i>	0	0.05	0.2	99.5	0.05	0.2		
9	<i>a</i>	31.0	35.2	3.8	27.7	2.3	0	2.61	1.0
	<i>b</i>	42.9	48.8	4.8	0	3.1	0		
	<i>c</i>	0	0.1	1.8	98.0	0.1	0.5		

Wherein, *a* is feed, *b* is distillate, *c* is column bottom liquor, EtAc is ethyl acetate, n-Hep is n-heptane, HAc is acetic acid, and HACr is acrylic acid.

- As is clear from the above table, the separability of acetic acid and acrylic acid varies according to the mol ratio of ethyl acetate to n-heptane. As shown in Experiment 5, in the case of ethyl acetate/n-heptane=1.7 (mol ratio), a considerable amount of acetic acid remains at the column bottom, but by making this ratio smaller, acetic acid does not remain at the column bottom but distills out from the column head, and acrylic acid is not contained in the distillate. Such an ideal or optimum ratio of ethyl acetate/n-heptane may be considerably affected by the concentrations of acrylic acid and acetic acid, but in the present example the ratio being in the preferred range of 0.2:1 to 1.5:1 is considered suitable, and in this case 99% of acetic acid could be removed from the column head almost without loss of acrylic acid.
- If the ratio is further reduced, as shown in Experiment 6, a larger amount of acrylic acid is contained in the distillate liquor.
- Experiments 7—9 show the cases where water is present. As shown in Experiments

7—9, the mol ratio of ethylacetate and water to n-heptane being in the range of 0.5:1 to 1.5:1 is also considered to be suitable.

5 This example and subsequent Examples were carried out with the addition of 0.2% of hydroquinone mono-methyl ether as a poly-

merization inhibitor.

Under the same conditions as in this Example, the direct separation of acrylic acid and acetic acid was carried out without using 10 n-heptane. The following result was obtained.

	Flow rate (g/H)	Composition (% by weight)		
		Acrylic acid	Acetic acid	Other heavy substances
Feed	25.0	84.0	16.0	—
Distillate	5.8	44.3	55.7	—
Bottom	19.2	95.4	4.1	0.5

15 In the above case, it is obvious that the separation is incomplete, compared with that of the azeotropic distillation.

#### EXAMPLE 2

20 The separation of acetic acid and acrylic acid was carried out by azeotropic distillation with the same distilling column as in Example 1, using n-heptane as entrainer.

25 The distillation was continuously carried out under a pressure of 175 mmHg abs. The feed liquor, consisting of 84% of acrylic acid and 16% of acetic acid, was pumped into the column at a point 2/3 up from the column bottom at a flow rate of 25.0 g/Hr., while maintaining the column bottom liquor at 100°—101°C and adding n-heptane at the top of column with reflux at the rate of 13.4 g/Hr.

30 The distillate liquor was countercurrently washed with water at a rate of 8.8 g/Hr. in a two stage mixer settler and the aqueous layer obtained at a rate of 13.7 g/Hr. had the following composition.

Acrylic acid	6.0%
Acetic acid	29.3%
Water	63.2%
n-heptane	1.5%

40 The oil layer obtained after washing was almost entirely composed of n-heptane and this, with a little water, was recycled as the refluxing liquor while supplementing n-heptane corresponding to the small amount thereof which had passed into the aqueous layer.

45 The small amount of n-heptane contained in the aqueous layer can be recovered by known methods; recovery was not undertaken in the present Example.

50 The column bottom liquor was obtained at a rate of 20.4 g/Hr. and its composition was as follows:

Acrylic acid	98.4%	
Acetic acid	trace	
n-heptane	0.6%	55
Other heavy substances	0.6%	

The yield of acrylic acid was 95.5%.

60 In the same way as in Example 2, azeotropic distillation was carried out but using n-heptane as an entrainer added at a rate of 20.0 g/Hr., together with water at a rate of 0.54 g/Hr. The following result was obtained.

	Flow rate (g/Hr)	Composition (% by weight)			
		Acrylic acid	Acetic acid	n-heptane	Water
Feed	25.0	84.0	16.0	—	—
Water washing*	13.1	0.8	30.6	1.5	67.2
Bottom distillate**	21.0	99.1	trace	0.5	—

\* Obtained by washing the distillate with water at a rate of 8.8 g/Hr.

\*\* Besides those mentioned, 0.6% of high boiling point substances were present.

In the above cases, the recovery of acrylic acid was 99.1%. Thus it appears that if the distillation is carried out by allowing water to be present in an optimum amount, the amount of acrylic acid in the distillate is reduced, thereby improving the effect of the separation.

#### EXAMPLE 3

Azeotropic distillation was carried out using n-heptane as an entrainer in the presence of acetonitrile under a pressure of 175 mmHg abs. with the same distilling column as in Example 1.

N-heptane saturated with acetonitrile (containing 2.5% of acetonitrile) was added at a rate of 15.9 g/Hr. from the top of the column with reflux.

The distillation was continuously carried out while feeding a solution consisting of 10.8% of acetic acid and 89.2% of acrylic acid at a rate of 34.8 g/Hr. into the column at a point 1/3 up from the column bottom, and as a result, a column bottom liquor was obtained at a rate of 30.4 g/Hr. and had the following composition.

Acrylic acid	99.3%
Acetic acid	trace
n-heptane	0.3%
Other heavy substances	0.4%

The distillate liquor was washed with acetonitrile containing 9.1% of n-heptane at a rate of 11.1 g/Hr. to obtain a washing liquor at a rate of 14.8 g/Hr. and of the following composition.

Acrylic acid	trace
Acetic acid	25.0%
n-heptane	6.7%
Acetonitrile	68.3%

The washing liquor was distilled by another

distillation column under normal pressure to obtain acetic acid from the column bottom. The distillate liquor was acetonitrile containing 9.1% of n-heptane and was recycled as washing liquor. The liquor washed with water was n-heptane saturated with acetonitrile and containing scarcely any acid; it was recycled as an entrainer for the azeotropic distillation column.

In the present Example, acrylic acid was refined with 99.3% yield, recovering high purity acrylic acid from the column bottom as well as scarcely distilling out any acrylic acid from the column head.

#### EXAMPLE 4

Azeotropic distillation was carried out using toluene as an entrainer in the presence of ethyl acrylate with the same distilling column as in Example 1.

The entrainer consisting 25.6% of ethyl acrylate, 72.7% of toluene and about 1.1% of water was added to the column at a rate of 18.0 g/Hr. under a pressure of 175 mmHg abs. from the top of the column with reflux.

The feed consisting of 10% of acetic acid and 90% of acrylic acid was fed at a rate of 25.0 g/Hr. into the column at a point 1/3 up from the column bottom. The distillation was continuously carried out to obtain a column bottom liquor at a rate of 22.5 g/Hr. and of the following composition.

Acrylic acid	99.1%
Acetic acid	trace
Toluene	0.4%
Other heavy substances	0.5%

The distillate was countercurrently washed with water at a rate of 6.3 g/Hr. with a two-stage mixer-settler to obtain an aqueous washing liquor at a rate of 8.8 g/Hr. and of the following composition.

5	Acrylic acid	trace
	Acetic acid	27.3%
	Water	71.4%
	Ethyl acrylate	1.2%
	Toluene	trace

sisting of 59.5% of ethyl acetate, 39.6% of n-heptane and 0.9% of water into the bottom of the column at the rate of 19.0 g/Hr., and maintaining the temperature at 30°C.

As a result, an extract liquor was obtained at a rate of 23.0 g/Hr. and of the following composition.

Acrylic acid	14.7%	35
Acetic acid	1.7%	
Ethyl acetate	47.1%	
n-heptane	32.6%	
Water	3.9%	

The aqueous washing liquor was returned to the top of the column as an entrainer with a make-up amount of ethyl acrylate corresponding to the amount thereof which had been transferred into the aqueous washing liquor.

In the present Example, highly pure acrylic acid was obtained from the column bottom with a recovery of 99.1%, and at the same time scarcely any acrylic acid was distilled out from the column head.

#### EXAMPLE 5

As an extraction column a packed column 270 cm high and 1.0 cm diameter (the same packing as in Example 1) was used. Extraction was countercurrently carried out while pumping an aqueous solution containing 25% of acrylic acid and 4% of acetic acid as the feed liquor into the column at a rate of 13.6 g/Hr. introducing an extraction solvent con-

The extract liquor was fed into the middle of a dehydrating tower and dehydrated by continuous distillation.

As the dehydrating tower, a triple tubular distilling column made of glass having an inside diameter of 2.0 cm and height of 120 cm (packed as aforementioned) was used. The distillation was carried out under normal pressure, with a reflux ratio of 0.5, a column head temperature of 67°–68°C and a column bottom temperature of 91°–92°C.

The following result was obtained.

	Flow rate g/H	Composition (% by weight)				
		Acrylic acid	Acetic acid	Water	Ethyl acetate	n-heptane
Distillate	10.6	—	—	0.85	68.8	22.7
Bottom	12.4	27.8	3.1	0.05	28.6	41.0

The distillation formed two liquid phases, the ratio of the organic layer to the aqueous layer being about 14:1.

Next, the bottom liquor from the dehydrating tower was fed into the middle zone of the solvent separation column and the separation of acrylic acid from the other components was carried out. As the solvent separation column, the same type of column as the de-

hydrating tower was used, but it was 200 cm high.

Azeotropic distillation was continuously carried out while pumping the feed into the middle zone of the column at a rate of 12.4 g/Hr. with a reflux of 0.8, under an operating pressure of 175 mmHg abs. and at a column bottom temperature of 100°C, the following result was obtained.

	Flow rate g/H	Composition (% by weight)				
		Acrylic acid	Acetic acid	Ethyl acetate	n-heptane	Other heavy substances
Distillate	9.0	—	4.2	39.3	56.4	—
Bottom	3.4	99.5	0.2	—	—	0.3

Thus, acrylic acid containing a very small amount of acetic acid and with a recovery yield of 99.3% could be obtained from the aqueous solution of acrylic acid.

When the organic layer of the distillate of the dehydrating tower and the solvent recovered from the residue of the extraction column by distillation (substantially ethyl acetate with a trace of n-heptane) and the organic layer of the distillate of the solvent separation column which contained acetic acid were combined together and further ethyl acetate and n-heptane corresponding to the amounts which had been lost during operation were added thereto and the whole was recycled as the extraction solvent, the concentration of acetic acid in the extract increased slightly to 2.1%, but the composition of the column bottom liquor of the solvent separation column was not affected by the recycling of the solvent.

#### EXAMPLE 6

An aqueous solution containing 20.0% of acrylic acid and 2.67% of acetic acid was introduced at a flow rate of 15.0 g/Hr. into the same extraction column as in Example 5 through the column head. A mixed solvent, of which the weight ratio of n-heptane to ethyl acrylate was 1:1, saturated with water,

was added at a rate of 21.0 g/Hr. at the column bottom. Liquid-liquid extraction was carried out at 30°C and as a result a extract liquor was obtained from the column head at a flow rate of 24.4 g/Hr. and of the following composition.

Acrylic acid	12.3%
Acetic acid	1.1%
Ethyl acrylate	42.1%
n-heptane	42.9%
Water	1.5%

Thus, in this extraction column, acrylic acid and acetic acid contained in an aqueous solution were extracted in 99.3% and 70% yield, respectively.

The extract liquor was fed directly into the same solvent separation column as in Example 5 and azeotropic distillation was carried out under a pressure of 175 mmHg abs., at a column bottom temperature of 100°C and with a reflux ratio of 1.3, to distil off solvent, water and acetic acid. The result was as shown below.

	Flow rate g/H	Composition (% by weight)				
		Acrylic acid	Acetic acid	n-heptane	Ethyl acetate	Water
Distillate	21.2	—	1.3	49.0	48.0	1.7
Bottom	3.01	98.9	0.3	0.05	0.3	—

Besides the constituents noted above, the column bottom liquor contained 0.4% of high boiling point substances.

As can be seen from the above, acrylic acid containing very small amounts of acetic acid was obtained with a recovery yield of 98.7% from the aqueous solution thereof.

#### EXAMPLE 7

To the column head of the same extraction column as in Example 5, as the feed liquor an aqueous solution containing 25.0% by weight of acrylic acid and 4.2% of acetic

acid was fed at a rate of 15.5 g/Hr. and was extracted at a liquor temperature of 30°C with a mixed solvent consisting of 53.5% of ethyl acetate, 40.1% of n-heptane and 4.4% of benzene at the rate of 19.7 g/Hr. The extract liquor was dehydrated in the same dehydrating tower as in Example 5 under normal pressure with a reflux ratio of 0.3. The bottom liquor of the dehydrating tower was azeotropically distilled in the same solvent separation column as in Example 5 under a pressure of 175 mmHg abs. with a reflux ratio of 0.7; the following result was obtained.

	Flow rate g/H	Composition (% by weight)						
		Acrylic acid	Acetic acid	Water	Ethyl acetate	n-heptane	Benzene	Other heavy substances
Feed	12.1	31.8	3.5	0.2	22.0	42.1	0.25	—
Distillate	8.23	—	5.0	0.2	32.2	62.2	0.36	—
Bottom	3.86	99.3	0.05	—	—	0.1	—	0.4

From the aqueous solution, acrylic acid was recovered in 99.1% yield.

#### EXAMPLE 8

- 5 To the column head of the same extraction column as in Example 5, as the feed liquor an aqueous solution containing 20.0% by weight of acrylic acid and 3.1% of acetic acid was fed at a rate of 16.8 g/Hr., extracted with  
10 a mixed solvent consisting of 59.1% of acrylonitrile, 39.4% of toluene and 1.5% of water
- at a rate of 19.2 g/Hr. and at a liquor temperature of 40°C. The extract liquor was then dehydrated in the same dehydrating tower as in Example 5 under normal pressure with a reflux ratio of 0.1. The bottom liquor of the dehydrating tower was azeotropically distilled in the same solvent separation column as in Example 5 under a pressure of 140 mmHg abs. with a reflux ratio of 1.2; the following result  
20 was obtained.

	Flow rate g/H	Composition (% by weight)					
		Acrylic acid	Acetic acid	Water	Acrylonitrile	Toluene	Other heavy substances
Feed	11.3	28.1	2.8	0.1	20.8	48.7	—
Distillate	8.12	—	3.9	0.1	28.2	67.7	—
Bottom	3.18	99.1	0.1	—	—	0.2	0.6

- From the aqueous solution, acrylic acid containing scarcely any acetic acid was recovered  
25 in 98.3% yield.

#### WHAT WE CLAIM IS:—

1. A method for refining acrylic acid which comprises removing acetic acid from a mixture of acrylic and acetic acids by azeotropic distillation at a pressure below 350 mmHg abs. and in the presence of a polymerization inhibitor, using as an entrainer an aliphatic or alicyclic hydrocarbon having 7 carbon atoms or toluene or a mixture thereof (the "first component"), together with water and/or an ester of the formula  $R_1COOR_2$  wherein  $R_1$  is a hydrocarbyl radical having 1—3 carbon atoms and  $R_2$  is a hydrocarbyl radical having 1—4 carbon atoms and the boiling point of which does not exceed 130°C and/or a nitrile having 3 or 4 carbon atoms (the "second component"), the molar ratio of the second component to the first component being in the range 0.05:1 to 1.5:1.  
35
2. A method as claimed in Claim 1 which  
45 comprises first extracting acrylic acid and acetic acid from an aqueous acrylic acid solution containing acetic acid using a solvent consisting of the first component as identified in Claim 1, alone or together with a second component as identified in Claim 1 and which is sparingly soluble in water, regulating the molar ratio of the second component (which may be water from the said aqueous solution) to the first component in the extract liquor to be in the range 0.05:1 to 1.5:1, and then subjecting the extract liquor to the said azeotropic distillation to remove the acetic acid.  
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3. A method as claimed in Claim 2 in which the extract liquor is treated in a dehydrating tower to distil out a part or all of the water and part of the solvent, and then, after regulating the molar ratio of the second component (which may be residual water) to the first component to within the said range, the resulting distillate liquor is subjected to the said azeotropic distillation to remove the acetic acid.  
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4. A method as claimed in Claim 2 or Claim 3 in which a major portion of the solvent is constituted by recycled distillate liquor from the (or each) distilling column.
- 5 5. A method as claimed in any of the preceding claims in which up to three tenths of the first component is replaced by benzene.
6. A method for refining acrylic acid substantially as described in any of the Examples.
7. A method for refining acrylic acid substantially as described with reference to the accompanying drawing.
8. Acrylic acid which has been refined by a process as claimed in any of the preceding claims.
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- 15

KILBURN & STRODE,  
Chartered Patent Agents,  
Agents for the Applicants.

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## COMPLETE SPECIFICATION.

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